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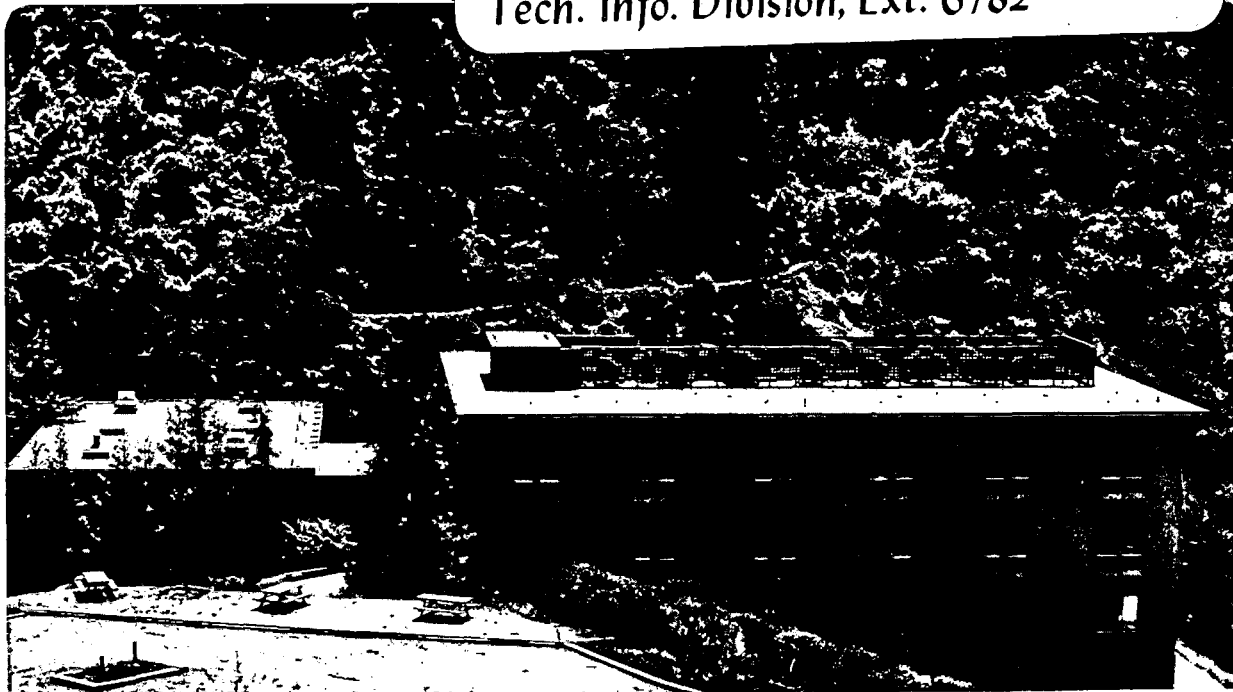
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DEUTERIUM ISOTOPE EFFECTS FOR HYDROCARBON REACTIONS
CATALYZED OVER PLATINUM SINGLE CRYSTAL SURFACES

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Abstract

The initial rates of hydrocarbon reactions of isobutane, neopentane, cyclohexane, n-hexane, and n-heptane, in the presence of deuterium, were measured over the flat (111), stepped (13,1,1), and kinked (10,8,7) platinum single crystal surfaces in the temperature range 520-650 K and at atmospheric pressures. Inverse isotope effects [$(R_D/R_H)=1.3-3.3$] were detected for a variety of hydrogenolysis, isomerization, and C₅-cyclization reactions. The inverse isotope effects that appear to arise from a combination of kinetic and thermodynamic isotope effects displayed magnitudes that were not much dependent on the platinum surface structure.

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Introduction

Important information about the elementary steps of catalyzed surface reactions involving hydrogen-containing molecules can often be derived from studies of deuterium isotope effects. As discussed by Ozaki¹, two major types of deuterium isotope effects can be distinguished: kinetic and thermodynamic. A kinetic isotope effect on the rate of reaction arises when rate constants differ for reactions carried out in hydrogen and deuterium or with deuterated reactants. Because deuterium makes larger contributions to translational and rotational partition functions than hydrogen, and because X-D bonds (X=C, M, O, etc.) possess lower zero point energies than X-H bonds, rate constants for deuterium addition and X-D scission are generally smaller than rate constants for H addition and X-H scission, respectively ($k_H > k_D$). Alcohol dehydration² and olefin hydrogenation³ are reactions which display kinetic isotope effects with magnitudes in the range $R_H/R_D = 1.5-4.5$

By contrast, thermodynamic isotope effects originate from a change in the equilibrium surface concentration of a reaction intermediate. Because of the lower zero point energies for X-D bonds, reaction intermediates that contain deuterium are expected to display larger adsorption equilibrium constants and higher equilibrium surface concentrations than reaction intermediates which contain only hydrogen ($K_{XD} > K_{XH}$, $\sigma_{XD} > \sigma_{XH}$). Detailed interpretation of these effects can be difficult because the thermodynamic isotope effect usually appears in combination with a kinetic isotope effect, i.e., $R_H/R_D = k_H \sigma_{XH} / k_D \sigma_{XD}$ ⁴. However, "inverse" deuterium isotope effects with magnitudes $R_D/R_H = 1.4-3.5$ have been clearly established for several types of reactions including CO-hydrogenation (deuteration) over silica supported ruthenium⁵ and ammonia (ND₃)-synthesis over unpromoted iron⁶. For these reactions, the thermodynamic isotope effects appear

appear to be larger than the kinetic isotope effects and, therefore, the reaction rates increase when the reactions are carried out in deuterium.

In the preceding paper, it was shown that n-hexane, n-heptane, and isobutane deuterium exchange reactions catalyzed near atmospheric pressure over platinum single crystal surfaces take place very rapidly as compared with the initial rates of hydrocarbon conversion reactions to form hydrogenolysis, isomerization, dehydrogenation and dehydrocyclization products. Provided that the reaction intermediates leading to hydrocarbon conversion in the presence of deuterium are partially deuterated, thermodynamic isotope effects should exist for the skeletal rearrangement reactions. Inverse deuterium isotope effects were, in fact, detected for a wide variety of reactions, and these isotope effects form the subject of this paper.

It was discovered that the rates of alkane hydrogenolysis, isomerization, and cyclization reactions catalyzed in excess deuterium at 500-650 K are about 1.4-3.0 times higher than the rates of the same reactions in hydrogen under identical experimental conditions. The magnitude of these isotope effects depend little on platinum surface structure and appear to decrease slightly with increasing temperature. A change in selectivity results when parallel reactions display deuterium isotope effects with different magnitudes.

Experimental

The apparatus, experimental procedures, and most of the materials used for the isotope effect studies were described in the preceding paper. All other reagents were of research purity; neopentane (Matheson, >99.98 mole %); cyclohexane (Phillips, >99.996 mole %); hydrogen (LBL-Matheson, >99.99 mole %). In addition to the flat (111) and kinked (10,8,7) platinum surfaces, a stepped

(13,1,1) surface was used in several experiments. This sample has terraces of (100) orientation that average seven atoms in width which are separated by atomic steps, one atom in height, of (111) orientation.

Isothermal retention times measured on a 0.19 % picric acid on 80/100 carbopack column were used to estimate the average deuterium content of the hydrogenolysis, isomerization, and cyclization products that were produced in the hydrocarbon conversion reactions. In the presence of deuterium, the gas chromatograph signals were always shifted 4-6 % towards shorter retention times as compared to the retention times that were measured in hydrogen. These shifts (mainly due to rotational entropy effects⁷) indicate that the reaction products were always extensively deuterated. The exchange distributions within the reaction products appeared to be narrow because the gas chromatogram peaks for each reaction product were always sharp, never broadened detectably, and always shifted by the same length of time independent of the reaction temperature and deuterium pressure.

Results

Scope of the isotope effect: Initial reaction rates in deuterium and inverse deuterium isotope effects (R_D/R_H) measured for a variety of hydrocarbon reactions catalyzed at 573 K over the flat (111), stepped (13,1,1), and kinked (10,8,7) platinum surfaces are summarized in Table 1. Magnitudes of the deuterium isotope effects were determined graphically by comparing the initial slopes of product accumulation curves determined as a function of reaction time in the presence of hydrogen and in deuterium. Example product accumulation curves for n-hexane isomerization to 2-methylpentane and cyclization to methylcyclopentane over Pt(111) are shown in Figure 1. Hydrogenolysis reactions of isobutane, neo-

pentane, n-hexane, cyclohexane, and n-heptane all displayed inverse isotope effects with magnitudes in the range $R_D/R_H = 1.3-1.8$. For isomerization reactions, the isotope effects were in the range $R_D/R_H = 1.2-3.3$. Isomerization of n-hexane to 2-methylpentane displayed the largest isotope effect $R_D/R_H = 3.0-3.3$; n-hexane isomerization to 3-methylpentane displayed a smaller effect ($R_D/R_H = 1.2-1.5$). Isomerization and hydrogenolysis of neopentane and isobutane displayed isotope effects with equal magnitudes on all surfaces investigated.

Cyclohexane dehydrogenation over Pt(111) exhibited a small inverse isotope effect ($R_D/R_H=1.2$). Aromatization of n-hexane and n-heptane on the (111) and (10,8,7) platinum surfaces displayed unique behavior characterized by small kinetic isotope effects ($R_D/R_H < 1$).

Temperature dependence of the deuterium isotope effects: The temperature dependence of the deuterium isotope effects was investigated carefully for n-hexane reactions catalyzed over the flat (111) and kinked (10,8,7) platinum surfaces. Arrhenius plots for these reactions catalyzed in hydrogen and in deuterium are compared in Figures 2 through 5. The error bars represent estimated uncertainties that are based on the reproducibility (about $\pm 15\%$) of the initial rate measurements. Hydrogenolysis and aromatization were the only reactions which displayed "normal" Arrhenius behavior over a wide range of temperature ($\sim 520-650$ K). Even for these reactions the apparent activation energies that were in the range 16-36 kcal/mole appeared to decrease with increasing reaction temperature. The other reactions (isomerization and C_5 -cyclization) displayed rate maxima at 570-630 K that were discussed in detail elsewhere⁸. Inverse isotope effects observed for hydrogenolysis appeared to decrease in magnitude with increasing temperature. No significant isotope effect was detected

for the aromatization reaction over either platinum surface. Figure 6 shows product accumulation curves for n-hexane aromatization catalyzed in deuterium at several temperatures on the (10,8,7) platinum surface. Reactions carried out in deuterium displayed deactivation behavior similar to that for reactions carried out in hydrogen. The rate of deactivation increased with increasing reaction temperature⁹.

Pressure dependence of the deuterium isotope effects: Initial reaction rates for n-hexane hydrogenolysis and aromatization catalyzed at 573 K on the (10,8,7) platinum surface are shown as a function of hydrogen (or D₂) pressure in Figure 7. The inverse isotope effect for hydrogenolysis displayed a nearly constant magnitude for all total pressures between 100 and 620 torr (i.e., $R_D/R_H = 1.4-1.8$). By contrast, the kinetic isotope effect for aromatization that was negligible at 100-220 torr increased markedly with increasing H₂-D₂ pressures reaching a value $R_D/R_H \sim 3$ for total pressures of 620 torr.

Isotope effects measured at several total pressures for cyclohexane dehydrogenation, ring opening, and hydrogenolysis catalyzed at 573 K on the (111) platinum surface are summarized in Table 2. These reactions displayed inverse isotope effects that decreased in magnitude with increasing pressure.

Discussion

Inverse isotope effects with magnitudes in the range $R_D/R_H = 1.3-3.3$ were detected for a variety of hydrogenolysis, isomerization, and C₅-cyclization reactions that were catalyzed over platinum single crystal surfaces in the presence of excess deuterium gas. Aromatization reactions displayed unique behavior characterized by a normal kinetic isotope effect $R_D/R_H < 1$. The magnitudes of all the isotope effects displayed little dependence on platinum surface structure. To the best of our knowledge, deuterium isotope effect for metal

catalyzed skeletal rearrangement reactions have not been considered previously.

Isotope effects measured for the hydrogenolysis and isomerization of isobutane and neopentane displayed equal magnitudes under all reaction conditions investigated. For these reaction, the selectivity was unaltered by the presence of deuterium. However, with n-hexane and n-heptane as reactants, parallel reactions usually displayed isotope effects with different magnitudes. In the presence of deuterium, the rate of formation of saturated hydrocarbon products was enhanced relative to the rate of formation of aromatics. As a result, the selectivities for these reactions were altered appreciably. This is shown clearly for n-hexane reactions catalyzed on the (10,8,7) platinum surface in Figure 8, where the kinetic selectivity for aromatization over hydrogenolysis in H_2 and D_2 is compared as a function of reaction temperature and hydrogen (D_2) pressure. The aromatization selectivity in deuterium was reduced over a wide range of reaction conditions. A similar effect was recently reported by Kellner and Bell⁵ for Fischer-Tropsch reactions catalyzed over silica and alumina supported ruthenium. In this case the kinetic selectivity for C_3 - and C_4 -olefin synthesis over C_3 - and C_4 -alkane production was lowered when the reaction rate studies were carried out in deuterium. Whereas the rates of formation of alkane products displayed inverse isotope effects with magnitudes in the range $R_D/R_H = 1.0-1.6$, the isotope effects for olefin production were always very small, $R_D/R_H = 1.0-1.2$.

A detailed model has been derived to rationalize the magnitudes of the observed inverse isotope effect⁹. Kinetic models for hydrogenolysis reactions developed by Leclercq et al.¹⁰, Cimino et al.¹¹, and Sinfelt¹² were employed for the analysis, as were "landing site" models^{13,14} for the reaction kinetics which allow for competitive chemisorption of the hydrogen, deuterium, and hydrocarbon reactants. The necessary Pt-H (Pt-D) stretching frequencies utilized in these

calculations were reported by Baro and Ibach^{15,16} and Primet et al.¹⁷. The analysis has confirmed that the measured isotope effects are reasonable and that they are consistent with each of the previously established kinetic models¹⁰⁻¹⁴ for the skeletal rearrangement of hydrocarbons. No meaningful distinction between the different mechanisms could be made on the basis of the isotope effects alone.

In addition, the analysis⁹ has revealed that the overall inverse isotope effects result from a combination of kinetic and thermodynamic isotope effects. Both effects appear to be important under the conditions of the experiments. A similar conclusion was reached by Kellner and Bell⁵ in connection with studies of co-hydrogenation (deuteration) over ruthenium catalysts. The importance of the thermodynamic isotope effect in the present research is clearly indicated by the facts that hydrocarbon-deuterium exchange was $10-10^3$ times faster than skeletal rearrangement¹⁸ and that all skeletal rearrangement products were extensively deuterated.

Acknowledgement

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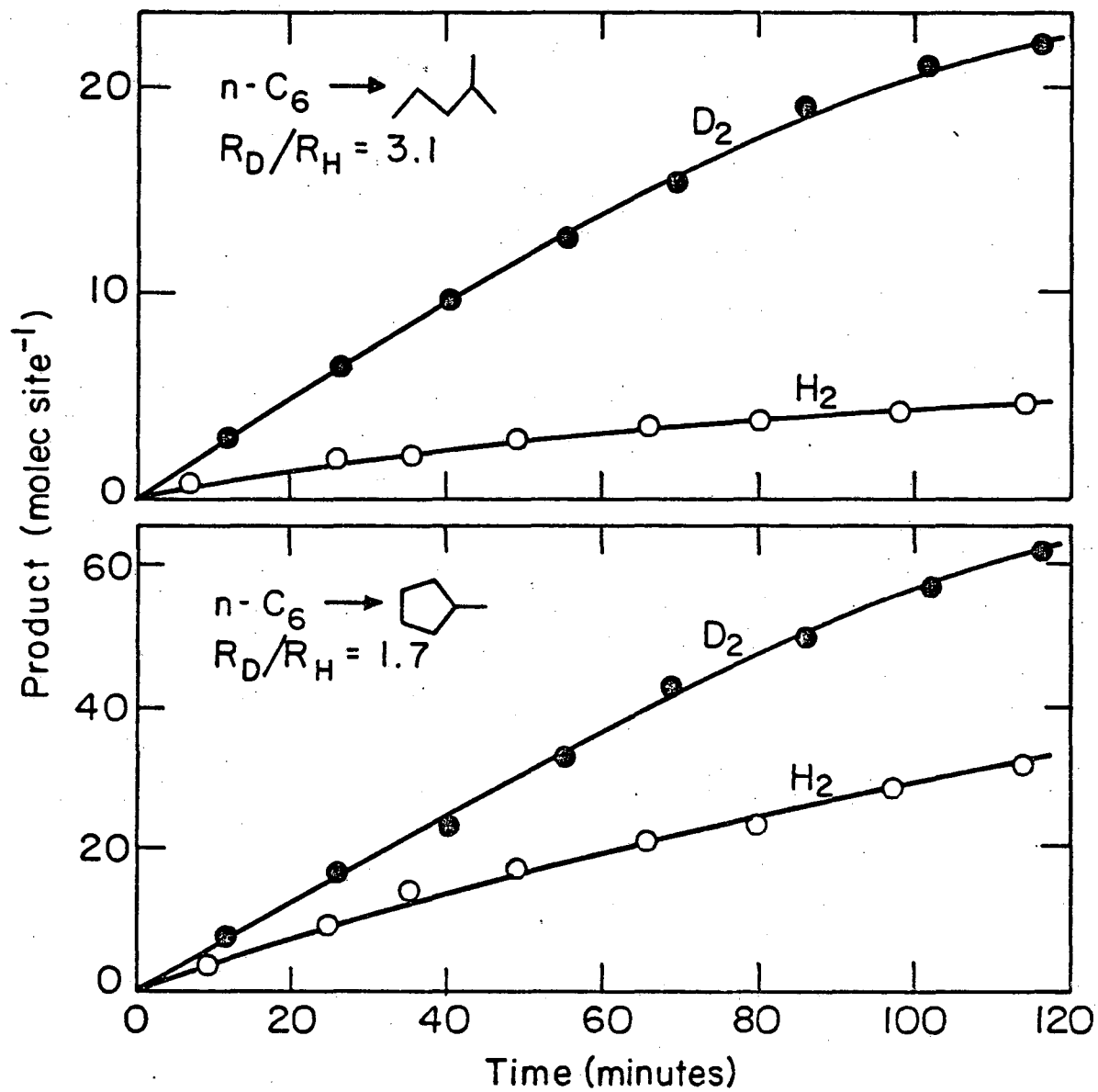
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Figure Captions

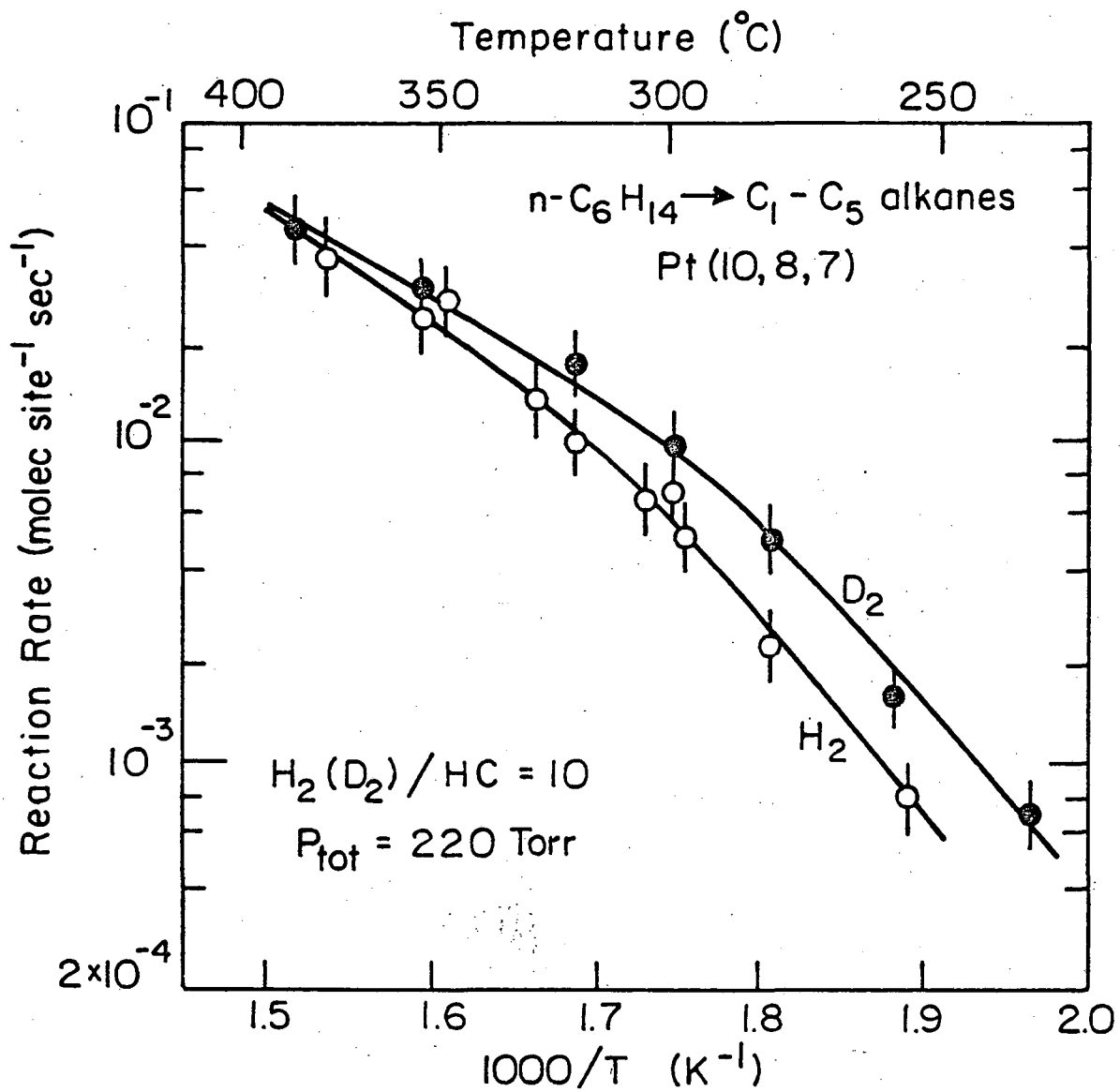
- Fig.1 Comparison between product accumulation curves determined in hydrogen and deuterium for n-hexane isomerization and C₅-cyclization catalyzed over Pt(111) at 573 K.
- Fig.2 Arrhenius plots for n-hexane hydrogenolysis catalyzed in hydrogen and deuterium over Pt(10,8,7,).
- Fig.3 Arrhenius plots for n-hexane aromatization catalyzed in hydrogen and deuterium over Pt(10,8,7,).
- Fig.4 Arrhenius plots for n-hexane hydrogenolysis and isomerization catalyzed over Pt(111).
- Fig.5 Arrhenius plots for n-hexane aromatization, C₅-cyclization, and isomerization catalyzed over Pt(111).
- Fig.6 Product accumulation curves determined as a function of reaction time for n-hexane aromatization catalyzed in deuterium over Pt(10,8,7).
- Fig.7 Comparison between n-hexane hydrogenolysis and aromatization rates as a function of hydrogen (deuterium) pressure.
- Fig.8 Initial kinetic selectivities for aromatization over hydrogenolysis determined for n-hexane reactions catalyzed in deuterium and hydrogen over Pt(10,8,7,). The selectivities are shown as a function of reaction temperature (upper frame), and hydrogen (D₂) pressure (lower frame).

20 Torr n-Hexane, 200 Torr H₂(D₂)
Pt(III) 300 °C



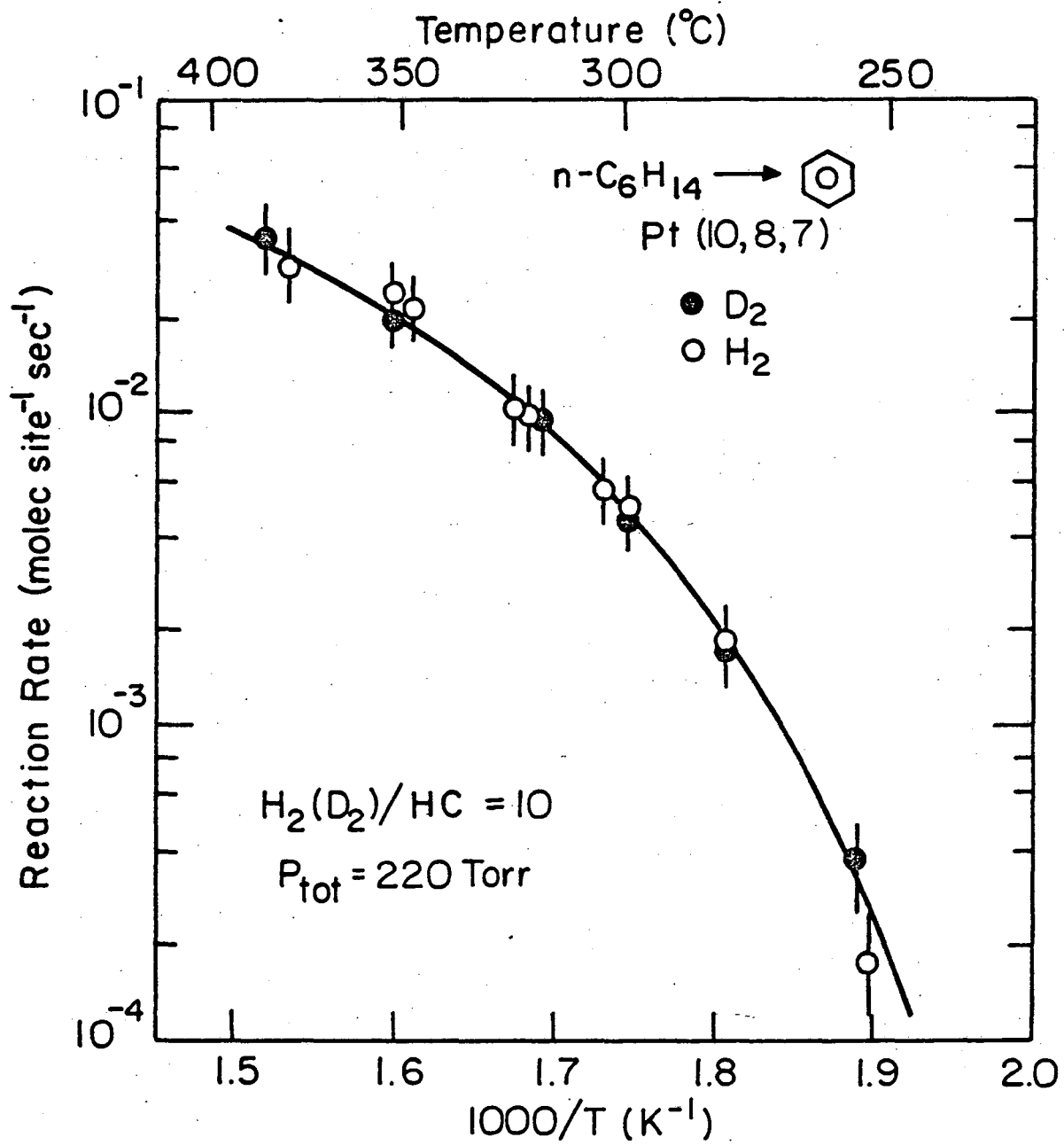
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Fig.1



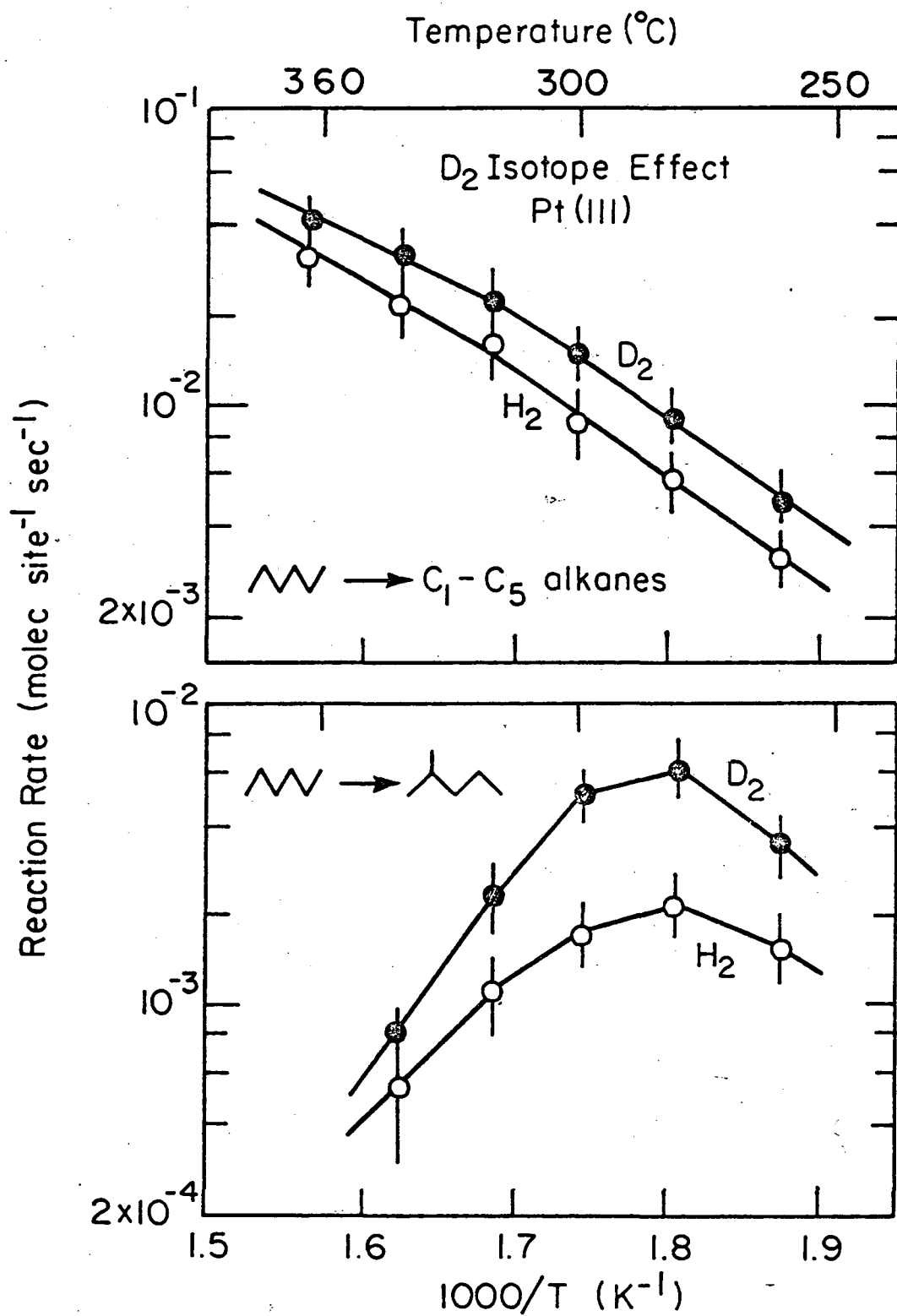
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Fig.2



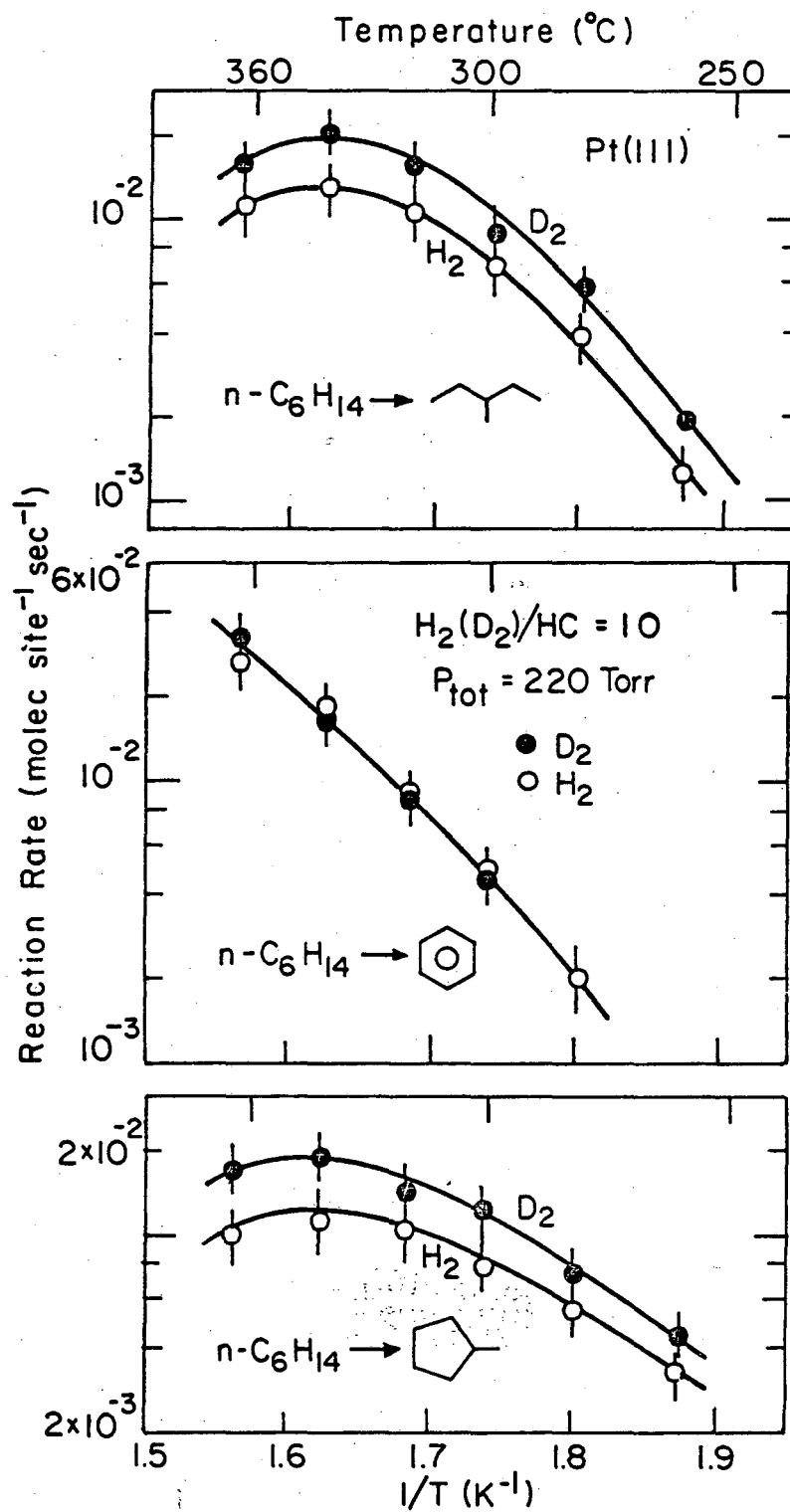
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Fig.3



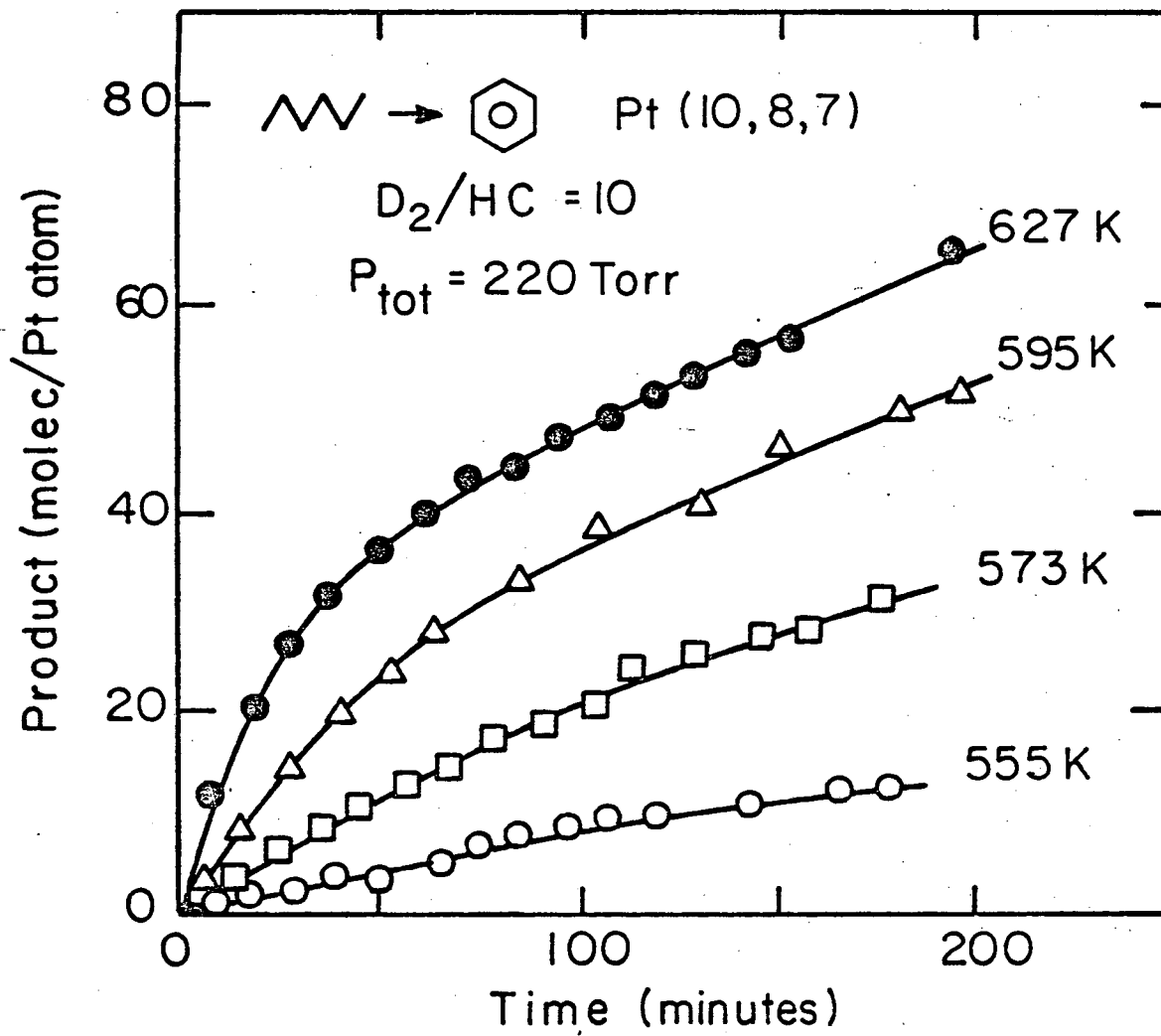
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Fig.4



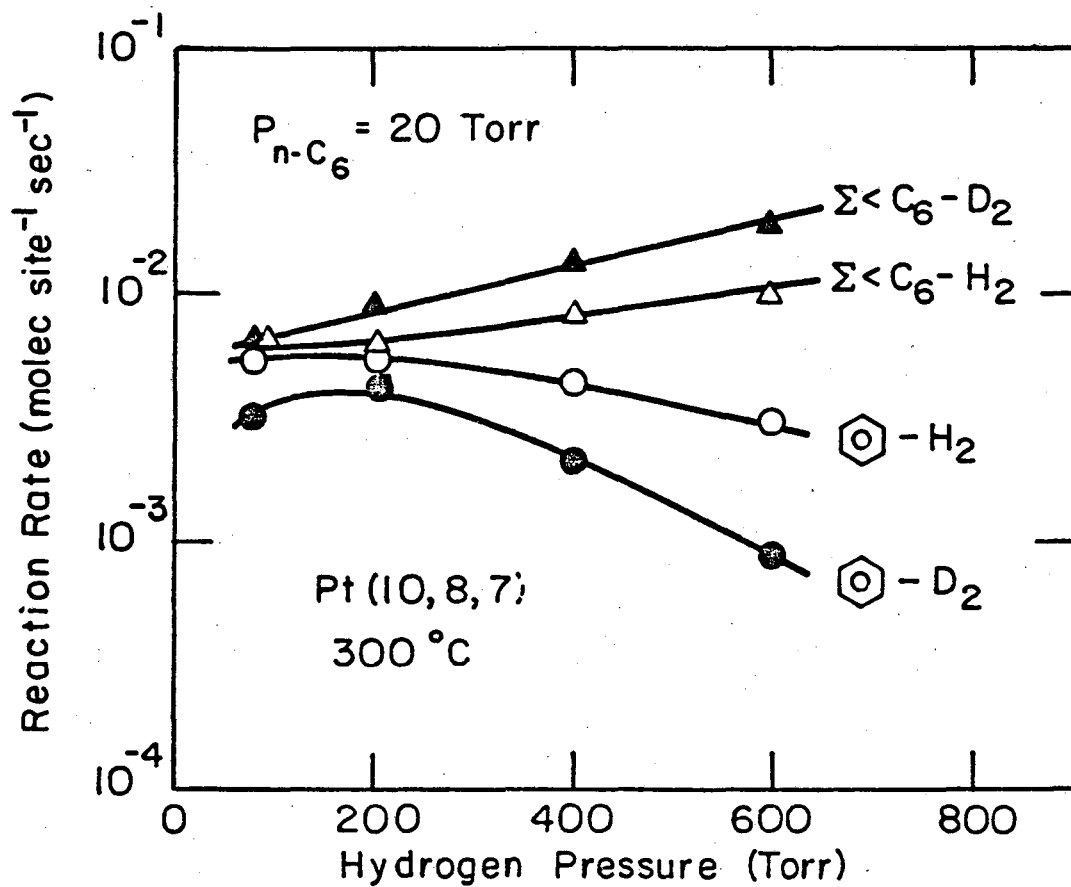
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Fig.5



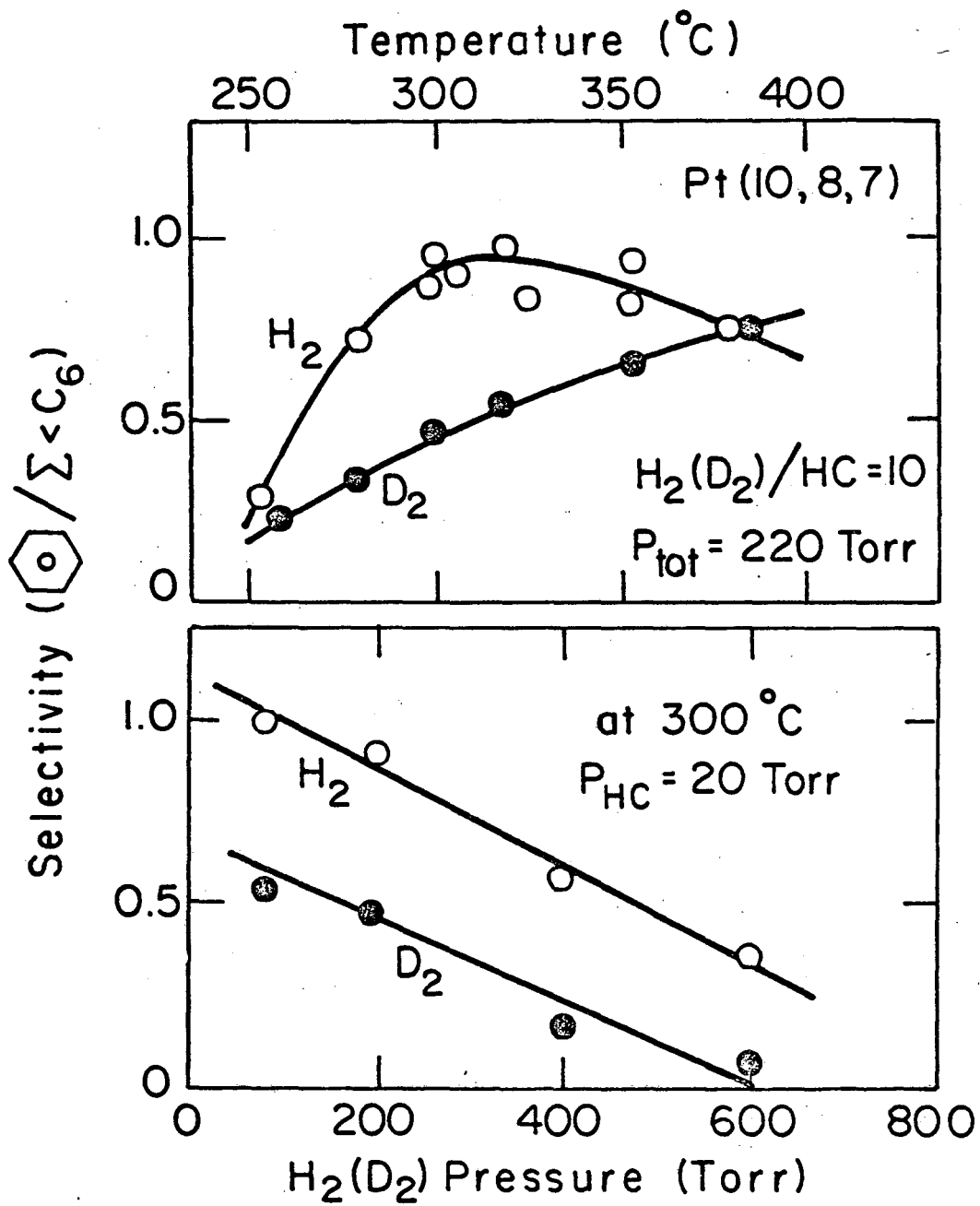
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Fig.6



XBL 8010-6077

Fig.7



XBL 815-5659

Fig. 8

Table 1. Initial Reaction Rates in Deuterium and Deuterium Isotope Effects Measured for Hydrocarbon Reactions Catalyzed at 573 K Over the Flat (111), Stepped (13,1,1), and Kinked (10,8,7) Platinum Single Crystal Surfaces^(a)

REACTANT	REACTION	INITIAL TURNOVER FREQUENCY (molec/Pt atom sec) ($\pm 15\%$)			INVERSE ISOTOPE EFFECT (R_D/R_H) ($\pm 30\%$)		
		Pt(111)	Pt(10,8,7)	Pt(13,1,1)	Pt(111)	Pt(10,8,7)	Pt(13,1,1)
Isobutane	Hydrogenolysis	0.0064	0.019	-----	1.8	1.4	-----
	Isomerization	0.053	0.075	-----	1.7	1.3	-----
Neopentane	Hydrogenolysis	-----	0.0047 ^b	0.048	-----	1.7 ^b	2.0
	Isomerization	-----	0.020 ^b	0.40	-----	1.5 ^b	2.0
Cyclohexane	Hydrogenolysis	0.005 ^c	-----	-----	2.0 ^c	-----	-----
	Dehydrogenation	9.6 ^c	-----	-----	1.2 ^c	-----	-----
n-Hexane	Hydrogenolysis	0.016	0.0089	0.013	1.8	1.4	1.9
	Isomerization	0.014	-----	0.0090	1.7	-----	2.1
	Cyclization	0.014	-----	0.018	1.7	-----	1.9
n-Heptane	Aromatization	0.0047	0.0042	-----	0.9	0.8	-----
	Hydrogenolysis	0.021 ^d	-----	-----	1.6 ^d	-----	-----
	Aromatization	0.0074 ^d	-----	-----	0.8 ^d	-----	-----

a) Reaction Conditions, $D_2/HC = 10$, $P_{tot} = 220$ Torr, 573 K

b) at 543 K

c) $D_2/HC = 6.7$, $P_{tot} = 115$ Torr

d) $D_2/HC = 32$, $P_{tot} = 495$ Torr

Table 2. Pressure Dependence of the Deuterium Isotope Effects Measured for Cyclohexane Dehydrogenation, Ring Opening, and Hydrogenolysis(a)

H_2/D_2 Pressure (Torr)	Inverse Isotope Effects (R_D/R_H) ($\pm 25\%$)		
	<u>Dehydrogenation</u>	<u>Ring Opening</u>	<u>Hydrogenolysis</u>
100	1.25	2.8	2.0
300	1.15	1.6	0.9
480	1.05	1.7	0.7

a) Pt(111) at 573 K, $P_{\text{HC}} = 15$ Torr

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